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Volume III	Ethylene Dichloride	Volume X	Ortho-Xylene
Volume IV	Benzene	Volume XI	Maleic Anhydride
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ASSESSMENT OF ORTHO-XYLENE

AS A POTENTIAL AIR POLLUTION PROBLEM

Volume X

by

Robert M. Patterson
Mark I. Bornstein
Eric Garshick

GCA CORPORATION
GCA/TECHNOLOGY DIVISION
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Michael Jones

EPA Task Officer

Justice Manning

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Volume XIII	Adipic Acid
Volume XIV	Phthalic Anhydride.

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SECTION I

SUMMARY AND CONCLUSIONS

Xylene is a colorless, flammable liquid having an aromatic odor similar to that of benzene and toluene. There are three isomers of xylene: ortho-, meta-, and para-xylene. Commercial xylene is a mixture of the three forms with meta-xylene being the major component and ortho-xylene making up about 20.5 percent of the mixture. Ortho-xylene is produced solely for the manufacture of phthalic anhydride, while mixed xylenes are used as solvents, for the manufacture of xylene sulfonates and xylidenes, and as high octane components of gasoline.

Data linking ortho-xylene exposure with health effects are lacking, due to the almost always concomitant benzene and toluene. Ortho-xylene is an irritant and narcotic at high concentrations, producing effects similar to alcohol intoxication. The NIOSH recommended standard for xylene is a time weighted average (TWA) exposure of 100 ppm for up to a 10-hour workday, 40-hour workweek, with a ceiling concentration of 200 ppm for 10 minutes.

Simple diffusion modeling estimates place the likely maximum 1-hour average ambient concentration at about 0.5 ppm of ortho-xylene. The maximum 24-hour average ambient concentration might be expected to be about 0.3 ppm.

About 1 billion pounds of isolated ortho-xylene were produced at nine locations in 1974, and production is expected to decline in 1975 before slowly increasing (6 percent growth by 1978). The primary emission

sources in descending order are mixed xylene solvent usage, mixed xylene production, ortho-xylene production and solvent usage, and bulk storage. Total emissions are estimated to have been about 184 million pounds in 1974.

Although emission controls specifically for ortho-xylene are not reported, two types of controls are used extensively by the chemical industry to control hydrocarbon emissions. These are vapor recovery and incineration. Control by adsorption on activated charcoal is used when recovery is economically desirable. The primary advantage of incineration is that low concentrations may be oxidized with only small supplemental fuel requirements. Fixed roof storage tanks can be controlled by venting to an adsorber or to an incinerator, or they can be converted to floating roof design.

Based on the results of the health effects research presented in this report, and the ambient concentration estimates, it appears that ortho-xylene as an air pollutant does not pose a threat to the health of the general population. In addition, ortho-xylene does not appear to pose other environmental insults which would warrant further investigation or restriction of its use at the present time.

SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Xylene is a clear, colorless, flammable liquid having an aromatic odor similar to that of benzene and toluene. There are three isomers of xylene, ortho (1, 2 dimethyl benzene), meta (1, 3 dimethyl benzene), and para (1, 4 dimethyl benzene). Commercial xylene is a mixture of the three forms with meta-xylene being the major component. Ortho-xylene is the subject of this report.

Commercial xylene is produced from both petroleum and coal tar. A typical petroleum product contains approximately 20 percent ortho-xylene, while approximately 10 percent-15 percent of xylene manufactured from coal tar consists of the ortho isomer. Essentially all xylene in the U.S. is produced from petroleum. Ortho-xylene is predominantly used in the manufacture of phthalic anhydride. Significant physical properties are listed in Table 1.[1]

HEALTH AND WELFARE EFFECTS

Effects on Man

Acute Poisoning - Xylene is an irritant to mucous membranes, and it is narcotic in high concentrations. Actual air concentrations have not, however, been reported when instances of acute poisoning have occurred. In one instance[2] three painters working in a ship's fuel tank were

overcome by xylene vapor from the paint they were using, in which the solvent was 90 percent xylene. The xylene concentration was estimated to have been 10,000 ppm. One of the men died shortly after discovery and an autopsy showed pulmonary edema and intra-alveolar hemorrhages. The other two men had temporary hepatic impairment and one had temporary renal impairment, but both recovered completely in two days.

Table 1. SIGNIFICANT PROPERTIES OF ORTHO-XYLENE[1]

Synonyms	Xylol, dimethyl benzene
Chemical formula	$C_6H_4 (CH_3)_2$
Molecular weight	106.16
Boiling point	143.6°C
Vapor density	1.024 (air = 1.0)
Solubility	Insoluble in water; miscible in alcohol, ether, and many organic solvents
Explosive limits	1%-6%
Flash point (closed cup)	17.2°C
Autoignition temperature	501°C
At 25°C and 760 mm Hg	1 ppm = 4.34 mg/m^3 1 mg/m^3= 0.23 ppm

Giddiness, anorexia (lack of appetite) and vomiting were observed in a paint-pot cleaner who used a solvent containing 75 percent xylene.[3] The remaining 25 percent was made up of ethylbenzene, methylethylbenzene, and trimethylbenzene. At head height above the pots the xylene concentration was 60 to 100 ppm when the pots were cold, and 270 to 350 ppm when they were warm. Higher concentrations were encountered when the painter placed his head inside the pots during cleaning.

For humans, only one report associates possible narcotic effects with a known concentration of xylene.[4] One of seven volunteers exposed to 230 ppm and one of six exposed to 460 ppm experienced slight lightheadedness without loss of equilibrium or coordination at the end of a 15-minute exposure period.

Ingestion of xylene has caused acute injury of the liver.[5] In one case a man mistakenly drank a small amount of nitrocellulose varnish, in which xylene was the main diluent, thinking it was water. He experienced immediate retro-sternal burning, heat and redness of the face, and some dyspnea (shortness of breath). Tests indicated toxic hepatosis with recovery in about three weeks.

Liquid xylene is also a skin irritant, causing erythema, dryness, and defatting. Prolonged contact can cause blistering, but absorption through intact skin is not significant.

Chronic Poisoning - The NIOSH recommended standard for xylene is a time weighted average exposure of 100 ppm for up to a 10-hour workday, 40-hour workweek, with a ceiling concentration of 200 ppm for 10 minutes.[6] This standard is based mainly on the narcotic and irritant actions of xylene.

Effects on Animals

Acute Poisoning - The acute oral toxicity of xylene to animals is less than that of toluene or benzene. The oral LD_{50} has been given as 1.85 ml/kg.[5] In white mice, narcotic effects have been noted at concentrations of about 4000 ppm of ortho-xylene, with a lethal concentration of about 7000 ppm.[7] A concentration of 3052 ppm of ortho-xylene for 24 hours was fatal to some mice.[8]

Chronic Poisoning - Rats, guinea pigs, monkeys, and dogs were exposed to 770 ppm of ortho-xylene for 8 hours a day, 5 days a week for 30 days; and to 78 ppm continuously for 90 days.[9] At the end of the exposures

the animals were killed. Sections of heart, lung, liver, spleen, and kidney were taken from all species; sections of brain and spinal cord were taken from dogs and monkeys. Results of microscopic examinations were negative and no significant changes were noted in body weight or hematologic data.

Effects on Vegetation

Tomato, barley, and carrot were exposed to xylene vapor at 1150 ppm for 1/4, 1/2, 1, and 2 hours.[10] Barley was the most sensitive while carrots were least sensitive, based on percent injury and time of recovery. The first noticeable symptom in all plants was a darkening of the tips of the youngest leaves, due presumably to a leakage of sap into the intercellular spaces. The darkening then spread to older leaves, and there was a loss of rigidity with drooping of stems and leaves.

AMBIENT CONCENTRATIONS AND MEASUREMENT

Ambient Concentration Estimates

Although ortho-xylene emissions are greatest from the solvent usage source category, these sources tend to be small and geographically scattered. Production of ortho-xylene, however, occurs at a few locations for which the emissions characteristics can be fairly well defined, and which as single point or area sources have a large emission density.

The largest installation for isolated ortho-xylene production is located near Houston, Texas, a city of over one million population, and it has a capacity of about 210 million lb/yr. Assuming a 0.5 percent loss, this converts to an emission rate of

$$\frac{(0.005 \text{ emission factor})\ (210 \times 10^6 \text{ lb/yr})\ (453.6 \text{ g/lb})}{3.1536 \times 10^7 \text{ sec/yr}}$$

= 15.1 g/sec of ortho-xylene.

Some assumptions must be made regarding this ortho-xylene release to the atmosphere. First of all, the emissions do not all come from one source location, but rather from a number of locations within the plant where ortho-xylene vapor leaks to the atmosphere. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Secondly, the emissions occur at different heights, and an average emission height of 10 meters is assumed.

Ground level concentrations can then be estimated at locations downwind of the facility.[11] To do this a virtual point source of emission is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100\text{m}/4.3 = 23.3\text{m}$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentration may be calculated from:

$$\chi = \frac{Q}{u\pi\sigma_y\sigma_z} \cdot e^{-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2}$$

or $$\chi = \frac{15.1}{(2)\ \pi\ (36)\ (18.5)}\ e^{-\frac{1}{2}\left(\frac{10}{18.5}\right)^2}$$

$$= 3.12 \times 10^{-3}\ g/m^3$$

for a 10-minute average concentration. Over a period of an hour this becomes $(3.12 \times 10^{-3}\ g/m^3)\ (0.72) = 2.25 \times 10^{-3}\ g/m^3$ or 0.5 ppm 1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to be about 0.3 ppm.

Ortho-Xylene Measurement Techniques

Analytical methods for measuring ortho-xylene concentrations in air include ultraviolet absorption spectrophotometry, colorimetry, and gas chromatography. Air is either drawn through a bubbler or passed over silica gel or charcoal to remove the ortho-xylene from the air. Sensitivity, specificity, and accuracy are functions of the sampling method used and of the sampling interval. Features of the techniques are discussed below.

Ultraviolet Absorption Spectrophotometry[12] - Ortho-xylene absorbs ultraviolet light at a wavelength of 272.0 mμ. Concentration may be determined by comparing the absorbance of the sample with the absorbance of known standards. In this technique air is collected in a gas washing bottle containing methanol, which is immersed in dry ice. After collection, the absorbance of ortho-xylene is determined on a spectrophotometer. This method is not specific for ortho-xylene as other aromatic hydrocarbons will interfere and is not sensitive enough for air pollution work. The lower detection limit is about 10 ppm of ortho-xylene.

Colorimetric Method[13] - In this technique air is collected in a special U-tube containing a solution of formaldehyde and sulfuric acid. After collection, the sample is transferred to a volumetric flask and diluted

with formaldehyde and sulfuric acid. The optical density of the color produced is read on a spectrophotometer at 460 mμ. The concentration of the sample is then read from a calibration curve. Concentrations from 40 to 350 ppm may be determined by this method. Interferences will result from other aromatic hydrocarbons. This method is not sensitive enough for air pollution work but may be used for industrial hygiene work.

Gas Chromatography[14] - Adsorption of xylene vapor on activated charcoal with subsequent desorption and analyses by gas chromatograph is the preferred sampling method for ortho-xylene. Concentrations in the range of 5 ppm are readily detectable by this method. Air is drawn through a tube containing charcoal on which organic vapors are adsorbed. The sample is then desorbed using carbon disulfide, and an aliquot of the desorbed sample is analyzed using a gas chromatograph. The presence and concentration of ortho-xylene are determined from its characteristic retention time and the area under the curve.

Interferences may result from other organic compounds having similar retention times; however, this may be overcome by changing the operating conditions of the instrument, usually the column and/or the column temperature.

This technique is especially well-suited for air pollution work since there is no requirement for special chemicals in the field.

SOURCES OF ORTHO-XYLENE EMISSIONS

Ortho-Xylene Production and Consumption - The production of isolated ortho-xylene in 1974 was 1,045 million pounds[15] and is expected to decline in growth during 1975 before slowly increasing (6 percent growth by 1978).[15,16,17] Because of economic conditions during 1974 production of ortho-xylene far exceeded its demand (789 million pounds). The only

outlets for ortho-xylene are for phthalic anhydride, exports and miscellaneous uses such as solvents for agricultural sprays. The difference between production and demand (256 million pounds) could not be accounted for even though conversations were held with several individuals in the chemical industry.[17,18,19] The only satisfactory explanation for the difference is that the ortho-xylene produced in 1974 was not all consumed and is being stored for future use when economic conditions improve.[20]

Presently, there are nine companies at nine locations who isolate ortho-xylene from unmixed xylene (see Appendix A). The consumption of isolated ortho-xylene for final products is shown in Table 2.

Table 2. ESTIMATED ISOLATED ORTHO-XYLENE CONSUMPTION - 1974

Product	Million pounds
Phthalic anhydride	667
Exports	117
Miscellaneous	5
Increase in inventories	256
Total	1,045

Ortho-Xylene Sources and Emission Estimates

In this report primary sources of emissions of ortho-xylene are estimated from both unisolated ortho-xylene present in mixed xylene streams, and from isolated ortho-xylene. Ortho-xylene is produced solely for the manufacture of phthalic anhydride; however, it is also a major component in mixed xylene streams. The composition of a typical mixed xylene has been reported[21] as shown in Table 3.

Mixed xylenes are used primarily to produce the individual isomers, for solvent usage and for the manufacture of xylene sulfonates and xylidenes. They are also used as high octane components of gasoline. See Table 4.

Table 3. AVERAGE COMPOSITION OF MIXED XYLENE[21]

Toluene	2.9%
Ethylbenzene	23.7%
p-xylene	16.7%
m-xylene	35.7%
o-xylene	20.5%
C_9+ aromatic	0.5%
	100.0%

Table 4. ESTIMATED XYLENE CONSUMPTION - 1974[15,17,18,19,20,22]

Product	Million pounds	
1. Mixed xylenes		5,791
As a source of individual isomers	4,328	
Solvent usage	809	
Xylene sulfonates, xylidenes	35	
Blended into gasoline	619	
2. Ethylbenzene		500
3. Ortho-xylene		1,045
Phthalic anhydride	667	
Exports	117	
Miscellaneous solvent usage	5	
Inventory	256	
4. Meta-xylene		99
5. Para-xylene		2,684

Emissions of ortho-xylene result from mixed xylene solvent usage, mixed xylene production, ortho-xylene production, miscellaneous ortho-xylene solvent usage and bulk storage. Total emissions from all categories are estimated to be 184 million pounds with emissions from mixed xylene production and usage accounting for approximately 93 percent of all losses. See Table 5.

Table 5. SOURCES AND EMISSION ESTIMATES OF ORTHO-XYLENE - 1974

Source	Million pounds
Mixed xylene solvent usage	166
Mixed xylene production	6
Ortho xylene production	5
Miscellaneous ortho-xylene solvent usage	5
Bulk storage	2

The major source of ortho-xylene emissions results from its use as a solvent present in mixed xylene (20.5 percent). The chief outlet of mixed xylenes in the solvent market is for industrial paints and thinners. It is assumed that all ortho-xylene used as a solvent will evaporate to the atmosphere. In 1974 an estimated 809 million pounds of mixed xylenes were used for solvent purposes.[22] Converting this figure to ortho-xylene will result in emissions of 166 million pounds.

The second major source of emissions results from the manufacture of mixed xylenes. Ninety-nine percent of all mixed xylenes are recovered from petroleum sources and the rest are obtained as a by-product of coke-oven operations. Approximately 96 percent of the recovered xylene from petroleum sources is solvent extracted from reformate and the remaining 4 percent is solvent extracted from pyrolysis gasoline.

Since there are no emission data available concerning these processes, based on other similar processes,[23] it is estimated that 0.5 percent of production is lost as mixed xylene resulting in 29 million pounds. Ortho-xylene emissions account for 20.5 percent of this total or 6 million pounds.

The next major source of emissions is from the production of ortho-xylene. Using the same assumptions as above, 0.5 percent of production is lost resulting in 5 million pounds of ortho-xylene emissions.

The fourth major source of ortho-xylene emissions is from miscellaneous solvent usage. Conversations with the industry have indicated that approximately 5 million pounds of ortho-xylene were used during 1974 as either a solvent for pesticide applications or as a solvent for other specialized purposes.[16,18] Again it is assumed that all solvent is evaporated to the atmosphere.

The last primary source of emissions results from the bulk storage of ortho-xylene. Using the emission factors in AP-42 and assuming that all storage tanks are fixed roof tanks, 2 million pounds of ortho-xylene are emitted from bulk storage tanks.[23]

Data from a recent report on phthalic anhydride[24] have indicated that emissions of ortho-xylene from this process are negligible. Based on this report, it is assumed that phthalic anhydride production is not a primary source of ortho-xylene emissions.

ORTHO-XYLENE EMISSION CONTROL METHODS

The literature does not report specific control equipment for ortho-xylene emissions, but it does report on control devices for other similar hydrocarbons.[25] Two types of control devices are presently used by the industry to control hydrocarbon emissions: vapor recovery and incineration. Both systems have reported efficiencies of at least 95 percent.

Control of hydrocarbon emissions by adsorption on activated charcoal is generally applied when recovery of adsorbed material is economically desirable. Adsorption should be used when concentrations of hydrocarbons are greater than 2500 ppm.[26] Other applications are for the control of very low concentration hydrocarbons that are poisonous to catalytic incinerators and for collection and concentration of low concentration emissions for subsequent disposal by incineration. Cost data for the cases utilizing adsorption are presented in Tables 6 and 7. The three cases presented are adsorption with solvent recovery, adsorption with incineration, and adsorption with incineration plus heat recovery.

Control of xylene emissions by incineration or catalytic oxidation involves direct oxidation of the combustible portion of the effluent, the desired ultimate products being water and carbon dioxide.

The primary advantage of catalytic incineration is that extremely small concentrations of organics can be oxidized with only small amounts of supplemental fuel required. The main disadvantages are the higher capital cost and the poisoning of the catalyst by certain hydrocarbons. Cost data for thermal and catalytic incinerators with and without heat recovery are presented in Tables 8 and 9.[27]

Control of emissions from storage tanks will require the use of floating roof tanks or venting the emissions to the previously mentioned adsorber or incinerator. Emissions from fixed roof tanks can be vented to either system without any major increase in cost. If these systems are not available the fixed roof tanks should be switched to floating roof tanks resulting in a 67 percent reduction of emissions. Figure 1 provides estimated costs of various gasoline storage tanks.[27] These equipment cost estimates can also be applied to ortho-xylene. As can be seen, conversion of fixed roof to floating roof tanks by installation of internal floating covers is more economical than the installation of new pontoon floating tanks.

Table 6. ESTIMATED INSTALLED COSTS[a] OF ADSORPTION SYSTEMS[27]

Adsorber capacity, SCFM - based on 25 percent lower explosive limit	1,000	10,000	20,000
With solvent recovery, $	74,000	162,300	280,000
With thermal incinerator/ No heat recovery, $	89,500	202,000	344,000
With thermal incineration/ Primary heat recovery, $	101,500	255,000	431,000

[a]Costs updated to 1st quarter 1975.

Table 7. ESTIMATED ANNUAL OPERATING COSTS[a] OF ADSORPTION SYSTEMS[27]

Adsorber capacity, SCFM - based on 25 percent lower explosive limit	1,000	10,000	20,000
With solvent recovery, $/yr	13,200	10,479[b]	37,200[b]
With thermal incineration/ No heat recovery, $/yr	23,400	64,300	123,200
With thermal incineration/ Primary heat recovery, $/yr	25,600	82,000	141,600

[a]Costs updated to 1st quarter 1975.

[b]Indicates a savings.

Table 8. ESTIMATED INSTALLED COSTS[a] OF THERMAL AND CATALYTIC INCINERATORS[27]

Incinerator capacity, SCFM - based on 25 percent lower explosive limit	1,000	10,000	20,000
Installed costs, $			
Catalytic without heat recovery	43,500	272,000	504,600
Catalytic with primary heat recovery	54,100	306,000	573,900
Catalytic with primary and secondary heat recovery	68,300	361,800	666,400
Thermal without heat recovery	27,200	92,500	137,400
Thermal with primary heat recovery	40,300	144,200	232,600
Thermal with primary and secondary heat recovery	54,400	200,000	322,300

[a]Costs updated to 1st quarter 1975.

Table 9. ESTIMATED ANNUAL OPERATING COSTS[a] OF THERMAL AND CATALYTIC INCINERATORS[27]

Incinerator capacity, SCFM - based on 25 percent lower explosive limit	1,000	10,000	20,000
Operating costs, $/yr			
Catalytic without heat recovery	16,200	102,800	195,000
Catalytic with primary heat recovery	16,400	78,500	177,900
Catalytic with primary and secondary heat recovery	19,300	108,700	203,700
Thermal without heat recovery	12,000	54,300	96,700
Thermal with primary heat recovery	11,500	36,300	59,200
Thermal with primary and secondary heat recovery	14,400	50,800	84,500

[a]Costs updated to 1st quarter 1975.

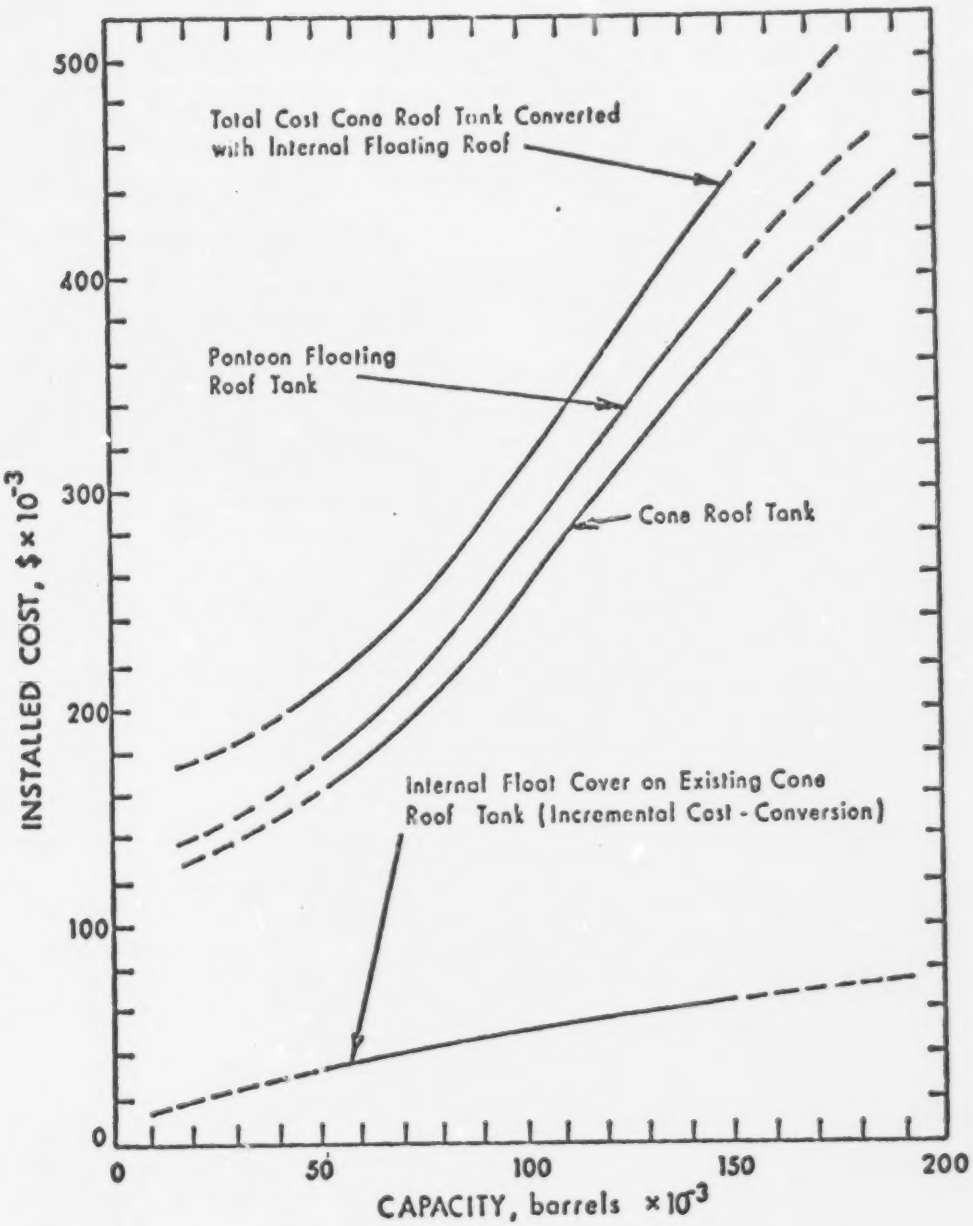

Figure 1. Estimated installed cost of ortho-xylene storage tanks (equipment costs assumed to be the same as gasoline storage tanks)[27]

SECTION III

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APPENDIX A

ORTHO-XYLENE MANUFACTURERS

		Annual capacity, million pounds
Arco	Houston, Texas	210
Chevron	Richmond, California	130
Commonwealth	Panuelas, Puerto Rico	150
Exxon	Baytown, Texas	130
Monsanto	Alvin, Texas	30
Phillips	Guayama, Puerto Rico	130
Shell	Houston, Texas	200
Sun	Corpus Christi, Texas	160
Tenneco	Chalmette, Texas	155
	Total	1,295